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(54) **Optical sensor for monitoring the partial pressure of oxygen.**

(57) A device is described for sensing oxygen, particularly for use in medical applications. The device includes an optical waveguide and an oxygen sensing medium disposed on the waveguide. The sensing medium fluoresces in response to light from a light source such that the intensity of fluorescnce is dependent on the partial pressure of oxygen in the environment. The sensing medium includes an oxygen sensitive fluorescent dye in a matrix consisting of a plasticized polymer.

EP 0 190 829 A2

describes the use of a two-fiber optical cable having a sensing tip consisting of perylene dibutyrate adsorbed on a powdered polystyrene support and enclosed in a gas permeable membrane. The dye is excited by light sent down one of the fibers. The resulting fluorescence is detected with the other fiber. Quenching of the fluorescence of perylene dibutyrate by oxygen is again used in this method.

Another general type of optical device for monitoring the partial pressure of oxygen can be based on the use of ruthenium (II) complexes as luminescent sensors. The properties of such complexes are described in Klassen et al., "Spectroscopic Studes of Ruthenium (II) Complexes. Assignment of the Luminescence", The Journal of Chemical Physics, Vol. 48, No. 4, (1968), Pages 1853-1858, and in Demas et al., "Energy Transfer from Luminescent Transition Metal Complexes to Oxygen", Journal of the American Chemical Society, Vol. 99, No. 11, (1977), Pages 3547-3551.

The use of perylene dibutyrate or pyrene dibutyric acid mounted on a solid support, or in solution, and enclosed in a membrane is unsatisfactory because of the complexity of fabrication and the poor sensitivity of the dyes. The luminescence of these dyes change substantially less than twofold when the partial pressure of oxygen changes from 0 to 760 mm. Hg. These changes have been measured and found to be only about ten percent or less. The ruthenium complex is much more sensitive than the other two materials, but is very slow to respond when used in the

The sensor described herein is particularly useful in multisensor systems for very small channels such as in arteries and in blood vessels, or in single-lumen medical catheters. The invention includes an optical waveguide to receive light transmitted from a light source. The invention also includes an oxygen-sensing medium disposed on the waveguide. The sensing medium fluoresces in response to light from the light source. The intensity of fluorescence of the sensing medium is dependent upon the partial pressure of oxygen present in the environment to be monitored. The sensing medium includes an oxygen sensitive fluorescent dye in a matrix consisting of a plasticized polymer.

An object of the invention is to provide a miniaturized oxygen sensor for medical applications.

Another object of the invention is to provide an oxygen sensor which is capable of responding to very small changes in the partial pressure of oxygen on the order of 1 to 5 mm Hg.

Another object of the invention is to provide an oxygen sensor which is easily fabricated and maintains its integrity during continued use.

Yet another object of the invention is to provide an oxygen sensor which is not susceptible to the effects of membrane contamination when used in medical applications.

These and other objects and advantages of the invention, as well as the details of an illustrative embodiment, will be more fully understood from the following description and the drawings.

FIG. 1 illustrates one embodiment of the sensor 10 in which a single optical fiber 12 having a core surrounded by a cladding is used. In this embodiment, a longitudinal portion of the cladding is removed to allow evanescent-wave light transmission from the core of the fiber to a sensing material 14. The sensing material and other aspects of this embodiment will be discussed in much greater detail below.

FIG. 2 illustrates another embodiment of the subject invention in which a sensor 16 includes a single optical fiber 18 which has a first end 20 which terminates in an acute angle to expose a portion of a core of the fiber 18. An oxygen-sensitive membrane 22 is applied to the first end of the fiber. In the preferred embodiment, the angle formed by the axis of light transmission through the fiber and the plane formed by the exposed portion of the core is thirty degrees. In other embodiments of the subject invention, the angle formed is generally less than sixty degrees. Experimental results indicate an angle which is substantially larger or smaller than twenty to thirty degrees tends to decrease the performance of the sensor. The performance is also affected by the smoothness of the exposed core surface.

FIG. 3 illustrates the light transmission characteristics and fluorescent characteristics of a typical sensor 24 fabricated in accordance with the subject invention. As can be seen from the figure, excitation light 26 and a fluorescent signal 28 both travel along the same optical fiber 30 so that extreme miniaturization or multiple sensors in a single small channel are possible. Experimental

blackened so as not to reflect light from the excitation light source into the signal detector.

In the preferred embodiment, the first end of the fiber is dipped into a solution consisting of tris (4,7-diphenyl-1,10-phenanthroline) Ru(II) perchlorate, polyvinyl chloride (PVC) and plasticizer (usually didecyl phthalate) dissolved in tetrahydrofuran (or any other solvent for PVC and the plasticizer used which will not attack the fiber core or cladding). The optimum composition appears to be, by weight: 0.0254 gm tris (4,7-diphenyl-1,10-phenanthroline) Ru(II) perchlorate, 1.00 gm PVC, 1.00 gm didecyl phthalate, and 25 gms of tetrahydrofuran. Adding more solvent causes a thinner, faster-responding coating but produces a less intense signal; adding substantially less solvent causes a thicker, slower-responding, less sensitive coating. The plasticizer is necessary to produce the fast response and, to some extent, the high sensitivity; too much plasticizer decreases the mechanical stability of the sensing coating. The phthalate class of plasticizers (didecyl-, dicyclohexyl-, and ditridecyl-, for example) seems to perform best. In the optimum embodiment described above, the plasticized polymer includes fifty weight percent of didecyl phthalate. If a substantially lower percentage of plasticizer is used, the response time of the resulting sensor becomes excessively long; on the other hand, if a substantially higher percentage is used, the resulting polymer film is undesirably soft and easily removed.

In other embodiments, the plasticizer may be selected from a group of materials consisting of

high degree, that it is compatible with the dye used, and that it can be dissolved in a solvent which will not attack the optical fiber used.

In some embodiments it is desirable to provide a gas-permeable, solution-impermeable sleeve about the optical fiber or waveguide. This is illustrated in phantom in FIG. 1 as element 32. In some embodiments the sleeve may be formed of polyethylene, polypropylene, or silicone rubber microbore tubing. The sleeve may be applied to the sensing device 10 by sliding a tube of the particular material used over the sensing device. In other embodiments, it is possible to apply the sleeve by coating the device with the material to be used and allowing the material to cure in place about the device.

FIG. 4 illustrates a Stern-Volmer plot showing the relative fluorescent intensity of light produced in a prior art sensor 34 and a sensor as described herein 36 as a function of the partial pressure of oxygen. A Stern-Volmer plot is a graph in which the fluorescence ratio of the sensor is plotted versus the percentage or partial pressure of oxygen. The fluorescence ratio (R) can be defined as:

$$R = (I_0/I_f - 1)$$

where I_o is the fluorescence at zero oxygen partial pressure and I_f is the fluorescence at a corresponding partial pressure of oxygen. As can be seen from the figure, the sensitivity of the device described herein is substantially greater than that of the prior-art sensor. The particular prior-art sensor that is used for comparison in FIG. 4 is a sensor of the type described above as developed by Demas and Bacon.

We Claim:

1. A device for monitoring oxygen in an environment in response to light transmitted from a light source comprising:

an optical waveguide to receive light transmitted from the light source; and

an oxygen-sensitive medium disposed on said waveguide wherein said sensitive medium fluoresces in response to light from said light source, the intensity of fluorescence of said sensitive medium being dependent on the partial pressure of oxygen present in the environment being monitored, said sensitive-medium including an oxygen-sensitive fluorescent dye in a plasticized polymer matrix.

2. A device for monitoring oxygen as recited in Claim 1, wherein: said plasticized polymer includes at least twenty-five percent plasticizer.

3. A device for monitoring oxygen as recited in Claim 1, wherein:

said oxygen-sensitive fluorescent dye includes tris (4,7-diphenyl-1,10-phenanthroline) Ru(II) perchlorate.

4. A device for monitoring oxygen as recited in Claim 1, wherein:

said oxygen-sensitive fluorescent dye is formed of any oxygen-responsive fluorescent salt of tris (4,7-diphenyl-1,10-phenanthroline) Ru(II) cation.

10. A device for monitoring oxygen as recited in Claim 1, wherein:

said plasticized polymer is plasticized with a derivative of phthalic acid, said derivative being compatible with said polymer.

11. A device for monitoring oxygen as recited in Claim 1, wherein:

said plasticized polymer includes a plasticizer selected from the group of materials consisting of phthalic acid derivatives, citric acid derivatives, adipic acid derivatives, and sebacic acid derivatives.

12. A device for monitoring oxygen as recited in Claim 1, wherein:

said plasticized polymer includes a polymer selected from the group of materials consisting of polyvinyl chloride, polystyrene, polyurethane, polyvinyl butyral, polymethyl methacrylate and silicone rubber.

13. A device for monitoring oxygen as recited in Claim 1, wherein:

said waveguide is a fiber optic waveguide having a core surrounded by a cladding, a portion of said cladding being removed from said waveguide to expose a portion of said core, said oxygen sensing medium being disposed on said exposed core.

14. A device for monitoring oxygen as recited in Claim 1, wherein:

said waveguide is a fiber-optic waveguide having first and second ends, said oxygen-sensing

said fiber having first and second ends, said first end terminating in a thirty degree angle to expose an elongated portion of said core; and

an oxygen-sensing medium composed of tris (4,7-diphenyl-1,10-phenanthroline) Ru(II) perchlorate dye in a matrix of polyvinyl chloride and didecyl phthalate, said matrix consisting of fifty-weight-percent polyvinyl chloride and fifty-weight-percent didecyl phthalate, said matrix being saturated with said dye, said oxygen sensing medium being disposed on said exposed portion of said core.

20. A device as recited in Claim 19, further comprising:

a gas permeable, solution impermeable membrane disposed about said fiber and said sensing medium.

21. A method for forming an oxygen sensor comprising the steps of:

immersing a portion of an exposed optical fiber core in an oxygen sensing medium dissolved in a volatile solvent, said solvent being unable to dissolve said fiber; and

allowing said solvent to evaporate to cause said oxygen sensing medium to dry to a solid phase.

22. A method for forming an oxygen sensor as recited in Claim 20, further comprising the step of:

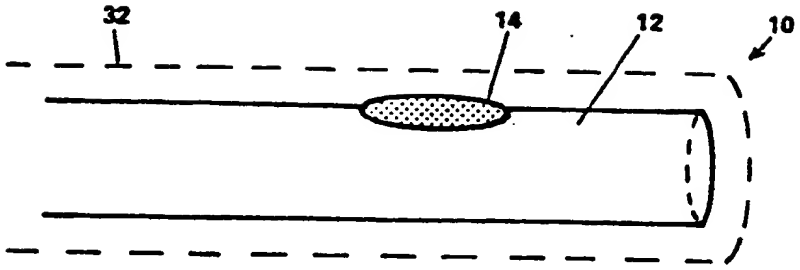

FIG. 1

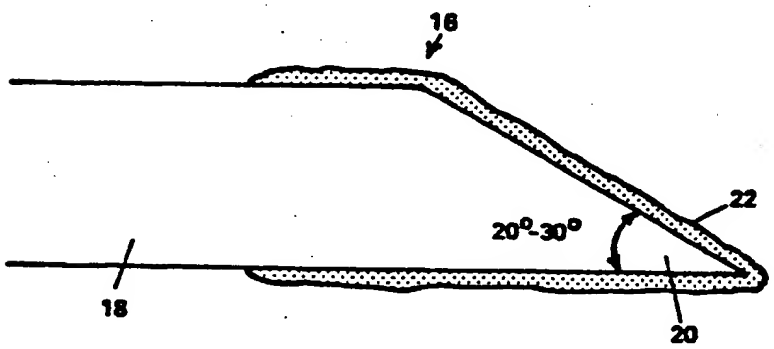

FIG. 2

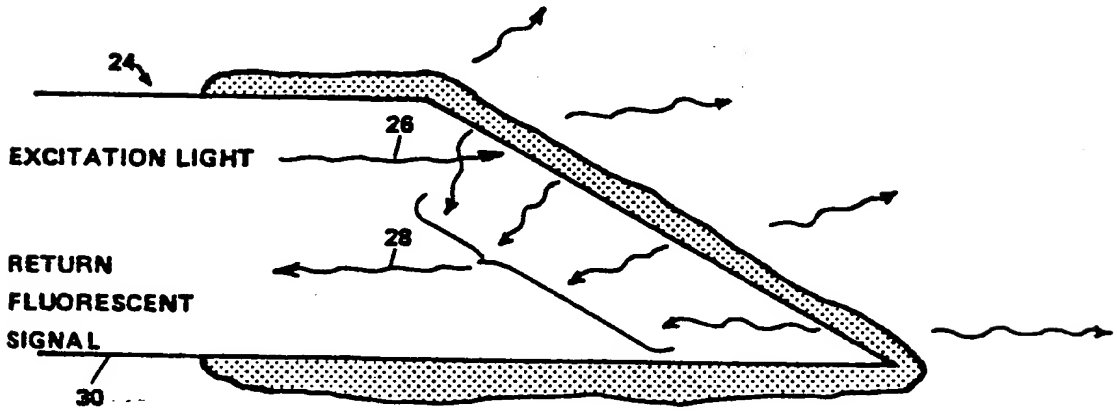

FIG. 3

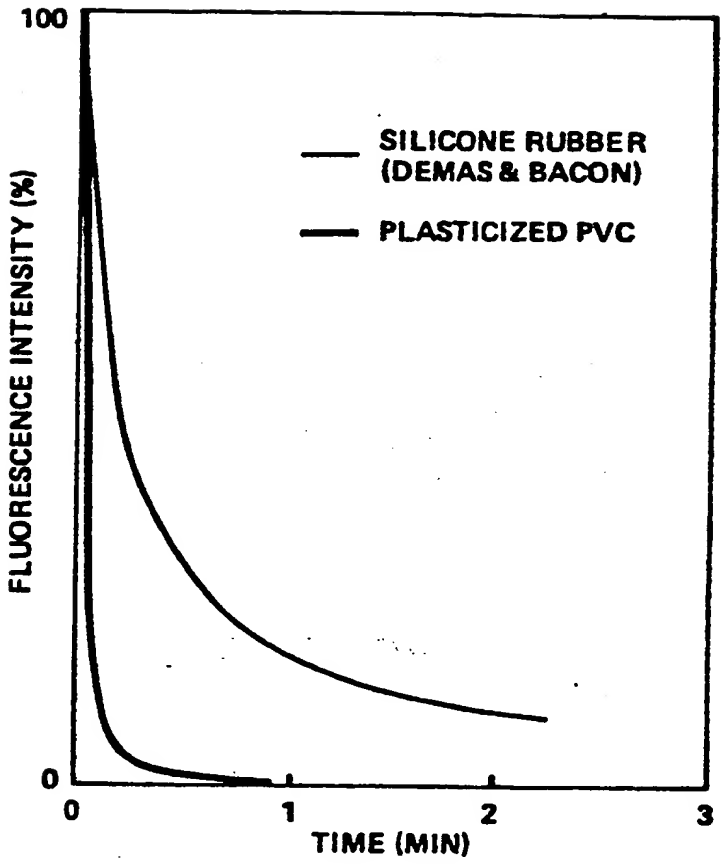

FIG. 5